

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

FAT SOLUBLE POLYMERS AND
THEIR USE IN FOODS

Background

Fat is an important part of the diet of all individuals.
5 It serves as a source of energy and essential fatty acids,
and also as a carrier for fat-soluble vitamins. In addition,
due to its unique functional properties, fat is often
used to improve the overall quality of foods including
color, texture, structure, flavor, mouthfeel and other
10 characteristics.

However, both the total desirable amount of fat and
types of fat in the diets of individuals have been a subject
of controversy. A number of investigations revealed a
correlation between high consumption of fats and increased
15 rates of atherosclerosis, coronary artery disease and
obesity. As a result, several organizations, including the
American Heart Association, U.S. Department of Agriculture
and Department of Health, have recommended the reduction of
total fat intake in general and of saturated fat in particu-
20 lar.

The nutritional and biological effects of fatty acids
are diverse. As long as 30 years ago, it was observed that
diets composed predominantly of saturated fatty acids
increased plasma lipids, whereas diets containing polyunsat-
25 urated fats decreased plasma lipids. More recent findings

-2-

indicate that even monounsaturated fatty acids, such as oleic acid, can be hypolipidemic. F.H. Mattson and S.M. Grundy, J. Lipid Res., 26:194 (1985). It is now well accepted that not only the total amount of fat, but also the composition of dietary fat which is consumed affects the incidence of coronary arterial disease.

The relative proportion of saturated to unsaturated fats consumed in the U.S. has changed significantly. The consumption of fats derived from vegetable oils that are rich in unsaturated fatty acids has more than doubled in the last 50 years. R.L. Rizek, et al., In Dietary Fats and Health, E.G. Health and W.J. Vesek, (eds.) American Oil Chemists' Society, Champaign, Il., p. 17 (1983). However, in a number of food products, the complete substitution of saturated fats with unsaturated fats is often problematic. The functional properties of fats in different foods are determined by a number of parameters, including the balance between solid and liquid phases and the structure of the fat crystal.

Fats can crystallize into different crystal forms. The consistency, plasticity, graininess, and other physical properties of many products such as butter, lard, margarine, shortenings, and cocoa butter, all depend on a particular polymorphic form of the triglyceride present. As a result, only a certain part of solid saturated fat can be substituted with liquid unsaturated oils without sacrificing the sensory quality of the product.

An alternative material that can mimic the physical and structural properties of saturated fats without having unfavorable nutritional qualities would be valuable for reducing the amount of saturated fat in a food product without sacrificing the sensory quality of the food product.

-3-

Summary of the Invention

The invention relates to an oil or fat which contains a polymeric, fat-soluble material and its use for the modification of the physical properties of fats and oils. The polymeric material be used in the present invention includes non-nitrogen containing, oil-soluble polymers, such as alkyd-type polyesters, polymers based on hydroxyacids and natural polymers, such as cutin, poly(vinyl esters), polyglycol esters and polyacrylates. Alkyd-type polyesters are particularly useful in the present invention.

The polymers are used in fat formulations wherein all or a portion of the fat is substituted by a mixture or an emulsion containing a liquid fat and the polymer. Naturally occurring oils, synthetic oils, fat mimetics or combinations thereof can be used in the present invention. In one embodiment, the polymeric, fat-soluble material is used as a texturing agent for oils. The polymer is added to neat oils to change the physical characteristics of the oils, such as the melting point and viscosity. Liquid oils composed of mostly unsaturated fatty acids solidify or form gels at room temperature in the presence of even small amounts of the polymer.

The polymer also helps to stabilize and solidify emulsions. In this embodiment, the polymer is incorporated into an oil-in-water or water-in-oil emulsion, forming a material having the physical and structural characteristics of saturated fat but which contains no saturated fat.

The present oils or emulsions treated with the oil-soluble polymers can be used to reduce the amount of saturated fat in foods. Use of the present treated oils or emulsions allows all or part of the saturated fat in a food to be replaced by unsaturated oils while still retaining desirable sensory or physical qualities of the food product.

-4-

Brief Description of the Drawings

Fig. 1 is a schematic representation of a polymer product made by the polycondensation of hydroxyacids.

Fig. 2 is a schematic representation of the structure
5 of cutin.

Fig. 3 is a schematic representation of a polymer formed by a polycondensation reaction between succinic anhydride and 1-monoglycerides.

Fig. 4 is a schematic representation of a polymer
10 formed by a polycondensation reaction between succinic anhydride and 2-monoglycerides.

Detailed Description of the Invention

Polymers useful in the present invention are non-nitrogen containing, oil-soluble polymers which when added
15 to a natural or synthetic liquid oil or fat, cause a change in the textural properties of the oil or fat. Polymers suitable for this purpose, for example, include natural polymers, such as cutin, polymers based on hydroxy acids, polymers prepared by the condensation of polyhydric alcohols
20 and polybasic acids, polymers derived from poly(vinyl alcohols), fatty acid esters of acrylates, and poly(ethylene glycol) fatty acid derivatives.

The term "oil-soluble" is intended to mean a polymer that is capable of dissolution or colloidal dispersion in an
25 oil medium under mild conditions without excessive heating or shear conditions. It is preferred that the oil-soluble polymers of this invention contain long chain, straight or branched alkyl substituents, for example, alkyl chains having 6 to 40 carbon atoms in length, with 8 to 30 carbon
30 atoms being preferred. The presence of the alkyl groups contributes to the oil thickening or emulsion thickening activity of the polymer.

-5-

Polymers which are particularly useful are members of the class of polymers generally known as "alkyd" polymers. Alkyd polymers are characterized in that they are generally prepared by reaction of a polyhydric alcohol, a polybasic acid and a fatty acid or an oil, usually in its monoglyceride form. Alkyd polymers can be prepared by any one of several known methods. For example, alkyd-type polymers were prepared by Van Bemmelen in 1856 by condensing succinic anhydride with glycerol. Van Bemmelen, J. Prakt. Chem., 69:84 (1856). In the so-called Fatty Acid method, a fatty acid, a polyol and an anhydride are mixed together and allowed to react. The Fatty Acid Monoglyceride method includes a first step of esterifying the fatty acid with glycerol, and when the first reaction is complete, adding an acid anhydride. The reaction mixture is then heated and the polymerization reaction takes place. In the Oil Monoglyceride Method, an oil is reacted with glycerol to form a mixture of mono, di, and triglycerides. This mixture is then polymerized by reacting with an acid anhydride. Parkyn B., Lamb F. and Clifton B.V., Polyesters (1967), Iliffe Books, London, Vol. 2; T.C. Patton, In: Alkyd Resins Technology, Wiley-Interscience, New York (1962). Alkyd polymers made by these and other methods can be used in the present invention.

Glycerol is a commonly used polyhydric alcohol due to its abundance and cost. In addition to glycerol, a number of other polyols such as glycols, polyglycerols, polyglycerol esters, sugars and sugar alcohols can be used as starting materials for producing the present edible polymers. Monoglycerides, which contain reactive hydroxy groups and a fatty acid are particularly useful starting materials.

Polybasic acids which can be used include natural edible multifunctional carboxylic acids, such as, for

-6-

example, citric, succinic, malic, fumaric, maleic or adipic acid, or the corresponding anhydrides. A variety of fatty acid can be used in preparing alkyd polymers, for example, fatty acids which generally occur in vegetable or fish oils.

5 The composition, molecular weight, and viscoelastic properties of the resulting polymers depends on the choice of starting materials and on the synthetic method used. For example, the number of reactive hydroxy groups on the polyhydric alcohol will affect the properties of the
10 polymer. In general, the greater the number of reactive hydroxy groups, the more viscous, less soluble, harder and less flexible the polymer becomes. The glycols, for example, which have two reactive hydroxy groups, produce only straight chain, linear polymers, which are soft and
15 flexible. Glycerol has three reactive hydroxy groups, thus, reaction with a single molecule of dibasic acid leaves one reactive hydroxyl, which is available for crosslinking, and a three-dimensional network develops. Polyhydric alcohols having more than three reactive hydroxy groups would tend to
20 form an even tighter crosslinked network. In many alkyd polymers which are based on glycerol, for example, one hydroxyl group will be reacted with a fatty acid, and the other two will form the ester linkages with the acid. Thus, the properties of an alkyd polyester can also be modified by
25 the choice of fatty acid which is used.

 The choice of the polybasic acid also affects the properties of the polymer. Dicarboxylic acids or anhydrides are generally used to form the present polyester polymers. However, triacids can be used, which result in a polymer
30 containing a free carboxyl group, which can be crosslinked or be derivatized to impart desired properties to the polymer.

-7-

Finally, alkyd resins can be terminated using monohydric alcohols (e.g., diglycerides) or monobasic acids (e.g., fatty acids). The choice of the terminal groups will depend in part on the properties of the polymer. For example, 5 long-chain fatty acids are used where increased oil solubility is desired.

The polymers useful in the present invention can also be made from other starting materials which result in the formation of ester bonds. For example, the condensation of 10 hydroxyacids, such as gluconic acid, glucoheptonic acid or ω -hydroxy fatty acids with themselves or with the appropriate polyfunctional molecule for forming polyesters, can result in the desired oil-soluble polymers. A polymer prepared by the polycondensation of hydroxyacids is shown 15 schematically in Fig. 1. Cutin, a naturally occurring polymer of this type is shown in Fig. 2.

Alkyd-type polyesters formed by the reaction of natural dicarboxylic acids and monoglycerides are preferred. Natural dicarboxylic acids which are preferred include 20 citric acid, succinic acid, malic acid, fumaric acid, maleic acid and adipic acid. The corresponding anhydrides can be used in place of the diacids. Preferred monoglycerides are monoglycerides derived from natural vegetable oils such as sunflower oil, safflower oil, soybean oil, canola oil, olive 25 oil, peanut oil and corn oil. An alkyd-type polymer prepared by the condensation of citric acid and 1-monoglycerides is described in Example 1. An alkyd-type polymer formed by the condensation of succinic anhydride and 1-monoglycerides is shown schematically in Fig. 3. An 30 alkyd-type polymer formed by a condensation reaction between succinic anhydride and 2-monoglycerides is shown schematically in Fig. 4. Polymers having a molecular weight of at least 2000 daltons are particularly useful.

-8-

Alkyd-type polyesters are widely used by the coating industry in a variety of products including resins, enamels, varnishes and paints. In relation to food products, they are used as coatings for food containers, for deodorizing
5 coating paper, and for corrosion protection in the meat and dairy industries.

In addition to the polyester texturizing agents described above, other classes of oil-soluble polymers having oil thickening and/or emulsifying properties include
10 polyvinyl alcohol fatty acid esters (e.g., polyvinyl stearate) and crosslinked polymers thereof (e.g., sebacoyl chloride crosslinked poly(vinyl stearate)). These polymers can be prepared by polyvinyl alcohol condensed with a fatty acid, fatty acid chloride or fatty acid anhydride. Examples
15 of some fatty acids include oleic, palmitoleic, linoleic, linolenic, butyric, palmitic and stearic. Fatty alcohol esters of methacrylate polymers, such as polyhexadecylmethacrylate and polyoctadecylmethacrylate, can be used as texturizing agents. These polyacrylates are commercially
20 available but could be synthesized using known synthetic methodologies. Alternatively, polyglycol esters such as polyethylene glycol distearate, have suitable oil texturizing properties. Polyglycol esters that are suitable for this purpose are commercially available.

25 The unique feature of the polymers described herein is that their presence in natural or synthetic liquid oils, even in small amounts, changes the viscoelastic properties of the oil significantly. It has been discovered, for example, that the presence of about 5% by weight of a
30 polyester formed by the condensation of monoglycerides and citric acid, causes a liquid oil to thicken or gel. The viscoelastic properties of the resulting thickened or gelled mixture resemble that of partially hydrogenated fats.

-9-

Thickened or gelled mixtures made from liquid oils that have been treated with oil-soluble polymers can be used as a substitute for partly or fully hydrogenated fats in food products. The terms "fats" and "oils" as used herein are intended to embrace both the naturally occurring oils and fats, synthetic oils and fats and fat mimetics. Examples of natural oils include but are not limited to sunflower oil, safflower oil, soybean oil, canola oil, olive oil, peanut oil or corn oil. Some examples of synthetic fats suitable for use with the texturing agents of this invention have been reported in the following:

SYNTHETIC FATS

- | | | |
|----|-------------------------|--|
| 15 | EP 0451781A | Fat composition used in chocolates, containing 10-90% 2-unsaturated-1,3-saturated triglycerides and 90-10% triglycerides with total carbon number 24-46. |
| 20 | U.S. Patent No. 4847296 | Administration of structured lipids to prevent catabolism in subjects under metabolic stress. Triglyceride substituents include one C12 acid, one omega-6 or omega-3 acid, and one C6-C24 acid. |
| 25 | WO 8601715A | Structured triglycerides for administration to subjects under metabolic stress, where substituents in the 1 and 2-positions are saturated C6-C12 or monounsaturated C12-C18 fatty acids and substituent in the 3-position is a diunsaturated or triunsaturated C18 fatty acid. |
| 30 | | |
| 35 | U.S. Patent No. 3450819 | Treatment of fat malabsorption with mixtures of C6-C12 fatty acids or esters of said acids are not more than 5% by weight of fatty acids and ratio of C8 to C10 acids is at least 2:1. |

-10-

SYNTHETIC FATS

- | | | |
|----|----------------------------|--|
| 5 | U.S. Patent
No. 3537865 | Mixture of triglycerides useful as a cocoa butter substitute, containing stearoyl didecanoins and optionally stearoyl dioctanoins or tridecanoin. |
| 10 | WO 9103944A | Low calorie fat composition comprising triglycerides having saturated C16-C40 fatty acid residues in the 1 and 3-positions and C2-C5 acid residues in the 2-position. |
| | WO 9210105A | Low calorie triglycerides with long chain saturated fatty acid residues having 16 to 40 carbons and short chain acid residues having 2 to 5 carbons. |
| 15 | WO 9215200A | Margarines, shortenings and plastic fats, wherein the fat component comprises a blend of 20-75% liquid oil and 25-80% solid fat with saturated C16-C24 residues and 30-67 mole % C2-C4 acid residues. |
| 20 | U.S. Patent
No. 4871768 | Synthetic triglycerides wherein at least one substituent is an omega-3 fatty acid and at least one is caprylic or caproic acid. |
| 25 | U.S. Patent
No. 4906664 | Use of structured triglycerides for nutrition of cancer patients, wherein at least one substituent is a medium-chain fatty acid, at least one is an omega-3 long chain fatty acid, and the other is medium or long. |
| 30 | U.S. Patent
No. 4952606 | Structured triglycerides useful for nutritional applications, formed by transesterification of a mixture of 10-90% dairy fat, 10-50% additional medium chain triglycerides, and 0-80% additional long chain triglycerides. |
| 35 | WO 9012080A | Synthetic triglycerides useful for treatment of patients with intestinal problems, wherein 1 or 2 of fatty acid substituents have 2-5 carbon atoms. |

-11-

SYNTHETIC FATS

- 5 WO 8809325A A synthetic triglyceride for medical use, where the 1-substituent is a C8-C12 fatty acid residue and the 2-substituent is a highly unsaturated fatty acid residue with at least 18 carbon atoms.
- 10 WO 9109597 Use of triglycerides containing one or more linear saturated or unsaturated C16-C24 acyl groups as agents with biological effect on intestinal mucosa.
- 15 EP 0322027A Reduced calorie fats comprising at least 15% MML, MLM, LLM or LML triglycerides, where M=C6-C10 saturated fatty acid residues and L=C17-C26 saturated fatty acid residues.
- 20 EP 0390408A Confectionery product containing MLM and MML triglycerides, where M is a C6 to C20 saturated fatty acid residue and L is a C20 to C24 saturated fatty acid residue.
- 25 EP 0422490A Pharmaceutical composition for inhibiting cholesterol absorption, comprising a triglyceride fat comprising 5-70% C20-C24 saturated fatty acids.
- 30 U.S. Patent No. 4832975 Reduced-calorie fat with improved auto-ignition characteristics, containing at least 30% SUM and SMU triglycerides, not more than 18% MMM triglycerides and not more than 30% MMS, MSM, SSM, or SMS triglycerides, where S are C18-C30 saturated in fatty acid residues, U are C18-C22 unsaturated fatty acid residues, and M are C6-C10 saturated fatty acid residues.
- 35 U.S. Patent No. 4888196 Confectionery composition containing a reduced calorie fat comprising at least 85% MLM and MML triglycerides and not more than 5% LLM and LML triglycerides, where M is a C6-C10 saturated fatty acid residue and L is a C20-C34 saturated fatty acid residue.

-12-

SYNTHETIC FATS

- 5 U.S. Patent No. 5066510 Reduced calorie fat comprising at least 85% MLM and MML triglycerides and no more than 10% LLM and LML triglycerides, where M is a C6-C10 saturated fatty acid residue and L is a C20-C24 saturated fatty acid residue.
- 10 U.S. Patent No. 4607052 Structured triglycerides wherein the 1 and 3-substituents are C4-C18 saturated fatty acid residues and the 2-substituent is a C18-C22 polyunsaturated fatty acid residue.
- 15 EP 0427309A Use in anti-blooming chocolate fat compositions containing 2-10% 1,3-dibehenoyl-2-oleoyl triglyceride, 5-14% 1,3-dibehenoyl-2-linoleoyl triglyceride, and 2-10%, 1,3-dibehenoyl-2-linolenyl triglyceride.

Preferred synthetic fats are "synthetic triglycerides" which are defined herein as a triglyceride prepared by a
20 sequence of one or more chemical reactions including one or more esterification or interesterification reactions wherein the component fatty acid substituents are derived from more than one source, or including one or more reactions, other than or in addition to hydrogenation, which change the
25 structure of substituent fatty acids.

Fat mimetics can also be used and are defined herein as a substance which is not a triglyceride fat and which has a lower calorie value than a triglyceride fat, but possesses the organoleptic properties of a fat. Some examples of fat
30 mimetics have been reported in the following:

-13-

FAT MIMETICS

- | | | |
|----|-------------------------|---|
| | EP 0325010A | Nondigestible fatty acid esters of epoxide-extended polyols. |
| 5 | EP 0481717A | Polyoxyalkylene block copolymers esterified with fatty acids, useful as reduced calorie fat substitutes. |
| | U.S. Patent No. 4861613 | Food compositions containing fatty acid esters of epoxide-extended polyols. |
| 10 | U.S. Patent No. 4959466 | Polysaccharides partially esterified with fatty acids, useful as nondigestible low-calorie fat substitutes. |
| | EP 0194154A | 2,3,4-Tri(fatty acid) hexoses, useful as low calorie fat substitutes. |
| 15 | EP 9416670A | Low-calorie fatty acid esters of polydextrose. |
| | EP 0481523A | Propoxylated monoglycerides and diglycerides esterified with fatty acids, useful as fat mimetics, are partially digestible and heat stable. |
| 20 | U.S. Patent No. 4508746 | Foods containing tricarballylic acid esterified with saturated or unsaturated alcohols having 8-30 carbon atoms. |
| 25 | U.S. Patent No. 4840815 | Low calorie food compositions containing alkyl glycoside fatty acid polyesters having at least four fatty acid ester groups. |
| | U.S. Patent No. 4942054 | Use of alkyl glycoside fatty acid polyesters with at least four fatty acid groups as low-calorie fat substitutes. |
| 30 | U.S. Patent No. 4973489 | Fat substitute food composition containing fatty acid polyesters of polysaccharides with at least three monosaccharide groups. |
| 35 | U.S. Patent No. 4983413 | Low-calorie food products prepared by replacing a portion of the oil with an organopolysiloxane. |

-14-

FAT MIMETICS

- 5 U.S. Patent No. 4849242 A method for reducing the available calories in a food composition by replacing a portion of the oil with a fatty acid ester of a polyoxyalkylene.
- WO 9110368A A low caloric oil made by esterification of a linear polyglycerol with fatty acids.
- EP 0205273A Food compositions containing polyorgano-siloxanes as substitutes for fat or oil.
- 10 U.S. Patent No. 4925692 A low-calorie food composition containing a nondigestible liquid siloxane polymer and an anti-anal leakage agent.
- 15 U.S. Patent No. 2924528 An edible composition comprising the random esterified mixture of palmitic and stearic acids with propylene glycol.
- U.S. Patent No. 4582927 Synthetic oils comprising malonic acid or 2-substituted malonic acid esterified with long chain alcohols.
- 20 U.S. Patent No. 5015418 Edible fat mimetic acyl malate diesters with melting properties similar to cocoa butter, wherein the acyl group is oleoyl and the ester groups are palmityl or stearyl.
- 25 U.S. Patent No. 2962419 Low-calorie foods containing fatty acid esters of neopentyl alcohol, trimethylolpropane, trimethylolpropane, pentaerythritol, or dipentaerythritol.
- EP 0303523A Partially digestible carboxy/carboxylate esters useful as low-calorie fat substitutes.
- 30
- EP 0325463A Fat mimetic compositions comprising complex linked esters including two poly-functional ethers or esters linked by a polycarboxy function having a common aliphatic group.
- 35

-15-

FAT MIMETICS

- 5 EP 0325464A Fat mimetic compositions comprising complex polyol esters elaborated with fatty acid esters and/or residues of esters or ethers having an acid function.
- EP 0353012A Ether-bridges polyester compositions useful as fat mimetics wherein two multibasic acids are joined by an ether-like linkage.
- 10 EP 0392798A Foods comprising partially digestible sucrose fatty acid esters.
- EP 0405873A Fatty acid diesters of diols useful as partially digestible fat substitutes.
- 15 EP 0405874A Fatty acid diesters of C4-C10 diols useful as fat substitutes.
- U.S. Patent No. 4830787 Partially digestible carboxy/carboxylate esters useful as low-calorie fat substitutes.
- 20 U.S. Patent No. 4915974 Food compositions comprising as a fat replacement molecular weight 1000-5000 polyvinyl alcohol esterified with fatty acid.
- 25 U.S. Patent No. 4927658 Fat substitute compositions comprising two 1,1,1-tris(hydroxymethyl)ethyl, propyl, or butyl units joined by an ester bridge and esterified with dicarboxylate-extended fatty acids.
- 30 U.S. Patent No. 4927659 Fat substitute compositions comprising 1,1,1-tris(hydroxymethyl)ethane or propane fatty acid esters.
- U.S. Patent No. 4959465 Fat mimetic compositions comprising polyol esters elaborated with fatty acid groups and/or ester or ether groups having an acid function.
- 35 U.S. Patent No. 4992292 Fat substitute compositions comprising tris(hydroxymethyl)ethyl, propyl, or butyl units joined by a C1-C8 alkyl bridge and

-16-

- esterified with dicarboxylate-extended fatty acids.
- 5 U.S. Patent No. 4992293 Thioester derivatives useful as fat mimetics for reduced calorie food compositions.
- U.S. Patent No. 5006351 Low-calorie food compositions containing cyclohexane, cyclohexene, or cyclohexadiene diol fatty acid diesters.
- 10 U.S. Patent No. 5008126 Discloses edible fat mimetic long chain diol diesters of two fatty acids or two dicarboxylate-extended fatty acids separated by 0-2 methylene groups at one end of the chain.
- 15 U.S. Patent No. 5043179 Fat mimetic compositions comprising fatty acid triesters of triols.
- U.S. Patent No. 5045338 Secondary amide esters useful as reduced calorie fat substitutes in foods.
- U.S. Patent No. 5059442 Primary amide esters useful as reduced calorie fat substitutes in foods.
- 20 U.S. Patent No. 5063075 Amide ether derivatives useful as low calorie fat mimetics.
- U.S. Patent No. 5064678 Fat mimetic compounds useful in reduced calorie foods comprising linked multi-ester or multi-ether fragments joined by a polycarboxylate.
- 25
- U.S. Patent No. 5068119 Fat mimetic compositions having an acid-labile -O-C-O- linkage, useful in neutral or alkaline food compositions.
- 30 U.S. Patent No. 5068120 Low calorie fat mimetic amine ester derivatives.
- U.S. Patent No. 5093142 Alcohol amine ester derivatives as fat mimetic compounds for reduced calorie compositions.
- 35 WO 8901293A Partially digestible carboxy/carboxylate esters useful as low-calorie fat substitutes.

-17-

FAT MIMETICS

- 5 WO 9118078 Fat mimetic carboxy/carboxylate esters.
- 5 U.S. Patent
No. 5139807 Amide linked fat mimetics consisting of
fragments bearing ester, ether, and/or
amide groups joined by an aliphatic or
alicyclic group through at least one
amide linkage.
- 10 JP 3285994 Low-calorie triglycerides with branched-
chain fatty acids having a C12-C22 main
chain and an alkyl group at the 2 or 3
position.
- 15 U.S. Patent
No. 3649647 Mixed sugar alcohol esters comprising a
sugar alcohol having 5 or 6 carbon atoms
esterified with 1-3 moles of a higher
saturated fatty acid and at least one
mole of a lower saturated fatty acid,
useful as fat substitutes, particularly
cocoa butter substitutes.
- 20 EP 0415635A Fatty acid esters of alkoxyated polyols,
useful as low-calorie fat substitutes.
- 20 EP 0415636A Low-calorie foods containing a fatty acid
ester of an alkoxyated alkyl glucoside.
- 25 EP 0495553A Reduced calorie 1,2-propylene glycol
diesters, where one ester group contains,
a medium-chain C6-C12 saturated fatty
acid radical and the other ester group
contains a long-chain C20-C24 saturated
fatty acid radical.
- 30 U.S. Patent
No. 3579548 Glycerol esters of alpha-branched carbox-
ylic acids, useful as low calorie fat
substitutes.
- 35 U.S. Patent
No. 3600186 Low calorie foods wherein 10-100% of total
fat is a sugar fatty acid ester having at
least four fatty acid ester groups or a
completely esterified sugar alcohol fatty
acid ester.
- U.S. Patent
No. 3634397 Esters of polyol mono (acidic lipid)
esters, useful as synthetic fats.

-18-

FAT MIMETICS

- 5 U.S. Patent No. 4582715 Alpha-acylated triglycerides wherein at least one of the ester groups is an acylated alpha-hydroxy acid, and their use as low calorie fats in food compositions.
- 10 U.S. Patent No. 5059443 Low-calorie foods containing a fatty acid ester of an alkoxylated alkyl glycoside, wherein the alkoxyl groups are derived from ethylene oxide.
- U.S. Patent No. 5077073 Fat substitutes comprising an alkoxylated sugar or sugar alcohol esterified with 6-8 fatty acid groups.
- 15 WO 9204833A Food composition wherein fat ingredients comprise a di-fatty ketone.
- CA 1106681 Use of glycerol fatty alcohol diethers and their fatty acid monoesters as low caloric fat substitutes in foods.
- 20 U.S. Patent No. 0519980 Edible compound fat comprising a fatty substance and refined mineral oil.
- WO 93/00016 Sorbitol fatty acid esters with a degree of substitution of about 4, useful as low calorie fat substitutes.

25 Liquid oils are mixed with an amount of the polymer sufficient to thicken or texturize the oil so that it has the desired textural properties. The term "texturize" as used herein means that desired characteristics such as viscosity, melting point, structure or plasticity, are imparted to the material. Most liquid oils gel, for
30 example, in the presence of from about 2 to about 20% (by weight) of the polymer. The polymer can also be added to saturated or partially saturated fats such as hydrogenated (or partially hydrogenated) vegetable oil, butter fat or cocoa butter, to produce a fat-like mixture having a reduced

-19-

level of saturated fat. The viscoelastic properties of the resulting mixture resembles those of partially hydrogenated fats. The thickened oils can be used as a substitute for solid fat in the production of baked goods.

5 The modified oil materials formed from the mixture of the polymer and the liquid oil demonstrate extremely useful melting properties; for example, they have a melting point range of about 37-40°C, which approximates body temperature. In food products, particularly those based on fatty materi-
10 als, such as margarines, spreads or confections, a clean and rapid mouthmelt is desired. This rapid mouthmelt is characteristic of cocoa butter, which is a standard for blends incorporating saturated and unsaturated fats. The present invention can achieve the mouthmelt standard of cocoa butter
15 without the use of solid, saturated fats.

Products that currently contain added solid fats include, for example, spreads, margarines, baked goods, frostings, chocolate and ice creams. The amount of saturated fat in these and other fat-containing foods can be
20 reduced significantly by replacing all or part of the saturated fat with gelled oils made by the present method.

In one embodiment of the present invention, baked goods made with liquid oil stock and no structural fats are produced. In this embodiment, the hydrogenated or partly
25 hydrogenated fats are substituted with the present modified oils consisting of mixtures of liquid unsaturated oils with oil-soluble polymers. In this method, liquid oils are thickened or texturized by adding an amount of the oil-soluble polymer sufficient to cause the oil to thicken
30 to the desired degree, as described above. The thickened or gelled oils are used in place of some or all of the hydrogenated or partially hydrogenated fat in the recipe.

-20-

Solid fats (e.g., butter, margarine, shortening) are used in baking applications for a number of reasons. In stabilized-foam products such as cakes, breads and other baked goods, for example, solid fats affect the batter
5 viscosity, cell volume, cool texture and finished height of the product. In simple non-leavened food systems, such as flaky pie crust, the solid fat contributes significantly to dough lamella formation and subsequent flaky texture. The same results can be obtained if all or a portion of solid
10 fat is replaced with a texturized oil of the present invention.

In another embodiment of the present invention, high quality, low-fat spread emulsions made with liquid oil stock and containing no saturated fats can be produced.

15 An unexpected observation was made that oil-soluble polymers can stabilize emulsion without the use of other known emulsifying agents. The polymers stabilize the emulsions and change their melting properties. For example, a 1:1 mixture of water and liquid vegetable oil in the
20 presence of about 3% of an oil-soluble polymer (e.g., succinic acid/monoglyceride polyester) forms a stable, unpourable emulsion. Low-fat spreadable emulsions, of either the water-in-oil or oil-in-water type can be made, for example, using liquid oils which have been treated with
25 a small amount of the polymers. Oil continuous emulsions containing from about 20 to about 80% by weight oil which exhibit the desired type, viscoelastic and textural qualities, i.e., those analogous to solid fats can be produced by this method.

30 Key to the proper textural development of the spreadable emulsions is the combined action of the aqueous and oil gelling agents present in the mixture. The polymer is used as the gelling agent of the oil phase. It is not necessary

-21-

to use an aqueous gelling agent to thicken the aqueous phase when the polymers of this invention are used. However, an aqueous gelling agent can optionally, though not preferred, be used in the aqueous phase. Aqueous gelling agents which can be used include, for example, gelatin, xanthan gum, gum arabic, guar gum, pectin, algin, carrageen and cellulose derivatives. The oil phase comprises an oil which is liquid at room temperature having any desired degree of unsaturation, such as, but not limited to, olive, corn, sunflower, sufflower, soybean or canola oil. "Winterized" liquid oils, which are oils that resist crystallization at low temperatures, e.g., below 40°F, are preferred. The oil phase also includes the polymer, and, optionally, oil-soluble emulsifier(s), colors and flavors. The aqueous phase contains water and an aqueous gelling agent; and can optionally contain salts, milk solids and flavors.

The emulsions generally contain from about 30 to 80% by weight of the oil phase, and about 20 to 70% by weight of the aqueous phase. The oil phase contains from about 1 to 10% by weight of the polymer, and the aqueous phase contains from about 1 to 8% by weight of the aqueous-soluble gelling agent, if necessary.

The emulsion is made according to the following general procedure. The polyester polymer is dispersed in the oil phase and heated to a temperature of from about 40 to about 100°C, after which optional ingredients, such as flavors, colors and emulsifiers, are added. The aqueous phase is prepared by heating the water to a temperature of from about 50 to about 90°C and optionally adding a gelling agent (or following the suitable procedure for the particular gelling agent), after dissolution of which other optional ingredients, if any, are added. The entire aqueous phase is normally heated to a temperature of from about 60 to about

-22-

90°C for a short time to effect pasteurization. The aqueous phase is allowed to cool to no lower than approximately 50°C, and is mixed with the oil phase under conditions appropriate to form the emulsion.

5 The emulsion is assembled under shear, using a high speed mixture or homogenizer. In this process, the oil phase is agitated under shear in the receiving vessel and the aqueous phase is slowly added, forming an emulsion of the aqueous phase in a continuous external oil phase. When
10 the emulsification is complete, the vessel is placed in a chilled bath, about 0°C, and the homogenizer speed is reduced. The vessel is spun and the sides of the vessel are scraped to remove and distribute any cooled or crystallized material. The procedure is continued until the emulsion is
15 plasticized, that is until it displays a measurable yield point or until further cooling and mixing is difficult due to the system viscosity.

It is during the scraped surface heat exchange process described above that the polymer in the continuous oil phase
20 thickens the oil to a gelled state. Gelling of the aqueous phase inhibits the mobility of the water by drastically increasing the viscosity of the water phase due to the gelation process. The viscosity of the resulting emulsion at the point of removal from the process apparatus approxi-
25 mates that of a softened butter. The texture of the emulsion (i.e., hardness) gradually increases with refrigerated storage, and until it approximates that of soft spread products currently on the market.

The present invention allows products having character-
30 istics associated with solid fat to be made which completely lack solid fats. Solid fats are saturated or partially saturated fats which form a structure or crystalline network which lends texture and stability to conventional margarines

-23-

and spread products. In general, attempts at making spread emulsions without a small percentage of added structural fat result in a failed or unstable emulsion. The present method results in a stable emulsion containing no structural solid
5 fat.

The invention will now be illustrated by the following Examples. All molecular weights are weight averages unless otherwise stated and all percents are weight percents unless otherwise stated.

10

EXEMPLIFICATION

Example 1: Synthesis of alkyd-type polymer from mono-
glycerides and citric acid and preparation
of fat spread emulsion

Thirty one grams (31 g) of monoglycerides derived from
15 hydrogenated vegetable oil (Myverol 18-06, Kodak, Eastman
Chemicals Division, Kingsport, TN) were placed in a round-
bottom 100 mL flask and melted at 140°C. Ten grams of
citric acid monohydrate (Sigma Chemical Company, St. Louis,
MO) were then added under stirring. The above weight ratio
20 resulted in 1/1.75 molar ratio of citric acid to mono-
glycerides. Vacuum was applied (6-10 mm Hg) and the
temperature was raised to 180°C. After 30 minutes, 200 mg
of p-toluenesulfonic acid catalyst were added and the
reaction mixture was stirred at 180°C and under vacuum for
25 another 22 hours, forming a citrate polymer.

The polymer was cooled to room temperature, homogenized
to a powdered state and thoroughly washed with methanol to
remove the catalyst. The molecular weight of the resulting
polymer (determined by GPC with different MW polystyrenes as
30 standards) was found to be around 9,000. The product
melting properties were determined by differential scanning

-24-

calorimetry (DSC). The melting point was found to be about 49-51°C. Analysis of a 5% (by weight) solution of the polymer in canola oil revealed an endothermic peak at 40°C with an enthalpy of 2.1 Joules/gram (J/g).

- 5 The resulting citric acid polymer was then used to prepare a high quality fat spread emulsion using liquid oil stock, without adding structural or saturated fat. The emulsion consisted of an aqueous phase, including salts, gelling agent, milk solids and flavors, and an oil phase,
10 which included the polymer, emulsifier(s), color and flavor.

In the formulation, the following components were used to assemble the final emulsion:

	<u>% in Final Product</u>
<u>OIL PHASE</u>	
Canola oil (Procter & Gamble Co.)	37.4
Dimodan-0 emulsifier (Grindsted Co.)	0.5
Citric acid polymer	2.0
Color (1% soln Beta carotene)	0.05
Flavor (Givaudan F-9093)	<u>0.05</u>
Total	40%
<u>MILK PHASE</u>	
Water	55.48
Salt	1.0
Milk Solids (Carnation Co.)	1.0
Gelatin (Hormel, 250 Bloom)	2.5
Flavor, cream; (Quest, Inc.)	0.01
Flavor, butter; (Chris Hansen Labs)	<u>0.01</u>
Total	60%

The polymer was dispersed in the oil phase and heated to 100°C after which the flavor, color and emulsifier were

-25-

added. The aqueous phase was prepared by heating the water to 70°C and dispersing the gelling agent. Then the remaining ingredients were added. The entire aqueous phase was heated to 80°C for a short time to effect pasteurization.

- 5 The aqueous phase was allowed to cool to 50°C and mixed with the oil phase.

The emulsion was assembled under shear, using a polytron homogenizer. With the oil phase undergoing shear in the receiving vessel, the aqueous phase was slowly added, forming a continuous external oil phase. Care was taken to avoid the inclusion of air in the emulsion. When the emulsification was complete, the vessel was placed in a chilled bath, at 0°C, with the homogenizer speed reduced. The vessel was spun and the sides of the vessel were scraped to remove and distribute the cooled or crystallized material. The procedure was continued until further cooling and mixing by this method was impossible due to the system viscosity. The viscosity of the product at the point of removal from the process apparatus was that of a softened butter. The emulsion was placed in a refrigerator at 4°C and the hardness gradually increased with refrigerated storage, and until it approximated that of a soft spread product, e.g., margarine.

25 Example 2: Synthesis of Polymer Derived from Monoglycerides and Succinic anhydride and Preparation of Fat Spread Emulsion

Twenty grams (20 g) of monoglycerides derived from hydrogenated vegetable oil (Myverol 18-06, Kodak) were placed in a round-bottom 100 mL flask and melted at 140°C. Succinic anhydride (5.3 g; Sigma) was then added under stirring. The above weight ratio resulted a 1:1 molar ratio of succinic anhydride to monoglycerides. The temperature

-26-

was raised to 200°C and the reaction mixture was stirred at this temperature for 24 hours, forming a succinylated polymer.

The polymer was cooled to room temperature and homogenized to form a powder. The molecular weight of the resulting polymer as determined by GPC was around 8,900. The product melting properties were then determined by DSC. The product melted at 50°C. DSC scan of a 5% (by weight) solution of the polymer in canola oil revealed an endothermic peak at 39°C with an enthalpy of 2.0 J/g.

The polymer was then used to prepare fat spread emulsions with liquid oil and no structural or saturated fat. In the formulation, the following components were used to assemble the final emulsion:

	<u>% in Final Product</u>
<u>OIL PHASE</u>	
Canola oil	46.6
Dimodan-O emulsifier	0.5
Succinic acid polymer	2.5
Refined Lecithin (Nattermann)	0.2
Phospholipid, Inc.)	
Color (1% soln. beta-carotene)	0.05
Flavor (Givaudan F-9093)	<u>0.15</u>
Total	50%
<u>MILK PHASE</u>	
Water	44.96
Salt	1.5
Milk Solids (Carnation Co.)	1.0
Gelatin	2.5
Flavor, cream; (Quest, Inc.)	0.02
Flavor, butter; (Chris Hansen Labs)	<u>0.02</u>

-27-

Total

50%

The procedure to form the emulsion was the same as in Example 1. The viscosity of this product was that of a softened butter similar to that produced in Example 1. Its hardness slightly increased with refrigerated storage. No oil separation was observed after 1 week storage at 4°C.

Example 3: Synthesis of polymer derived from monoglycerides and malic acid and preparation of fat spread emulsion

Twenty eight grams (28 g) of monoglycerides derived from hydrogenated vegetable oil (Myverol 18-06, Kodak) were placed in a round-bottom 100 mL flask and melted at 120°C. Ten grams of malic acid (Sigma) were then added under stirring. The above weight ratio gives 1:1 molar ratio of malic acid to monoglycerides. Four hundred mg of p-toluenesulfonic acid catalyst were added to the reaction mixture, vacuum was applied (6-10 mm Hg) and the mixture was stirred at 120°C for 3 hr. It became important at this point to have precise temperature control, because malic acid decomposes at 140°C. During the next 4 hours, the temperature was raised slowly to 150°C. The reaction mixture was incubated for 1 hour, then heated to 180°C and kept at this temperature for another 15 hours forming the polymer.

The polymer was cooled to room temperature, homogenized and thoroughly washed with methanol to remove the catalyst. The molecular weight of the resulting polymer determined by GPC was around 6,400. The product melting properties were then determined by DSC. The melting point was found to be around 48°C. Scans of a 5% (by weight) solution of the polymer in canola oil revealed an endothermic peak around 30°C with an enthalpy of 2.7 J/g.

-28-

The polymer was then used to prepare fat spread emulsions with liquid oil stock and no structural or saturated fat. Composition of the phases and the preparation method was as described in Example 2. The resulting product was a firm stable butter-like emulsion. No oil separation was observed upon storage at 4°C for 1 week.

Example 4: Pie crust formulation using citrate polymer/canola oil emulsion

A citrate polymer was prepared as described in Example 1. It was then used in combination with canola oil as a substitute for CRISCO® brand shortening in pie crust. Positive and negative controls were used for comparison. The following formulation was used to make the pie crusts:

<u>Component</u>	<u>Test material</u>	<u>% in Final Product</u>	
		<u>Positive control</u>	<u>Negative control</u>
Shortening (CRISCO® Brand)	0	25.66	0
Canola Oil	0	0	25.66
Canola Oil containing 7% polymer	25.66	0	0
Flour	51.35	51.35	51.35
Salt	1.6	1.6	1.6
<u>Component</u>	<u>Test material</u>	<u>% in Final Product</u>	
		<u>Positive control</u>	<u>Negative control</u>
Ice water	21.39	21.39	21.39
Total	100	100	100

The polymer (7% by wt.) was dispersed in the canola oil and heated to approximately 100°C. The mixture was then cooled and stored at 4°C until use. Salt, flour and

-29-

the shortening or oil were mixed together in a bowl. Water was then added to form a dough. The dough was refrigerated for 2 hours, rolled into 1/8" thick circles and baked at 445°F for 8 minutes. Test material and positive control exhibit similar texture and flakiness, as well as similar in-mouth properties. The negative control was somewhat softer, flat and dense with poor in-mouth feel and little flakiness.

10 EXAMPLE 5: Synthesis of crosslinked polymer derived
from poly(vinyl alcohol) molecular weight
9000-10,000, stearyl chloride and sebacoyl
chloride.

15 Poly(vinyl alcohol), average molecular weight 9000-10,000 (880 mg, 20 mM based on vinyl alcohol; Aldrich Chemical Co.) was dissolved in dry N,N-dimethylformamide (10 mL). A mixture of stearyl chloride (6.06 g, 20 mM; Aldrich Chemical Co.) and sebacoyl chloride (48 mg, 0.2 mM; Aldrich Chemical Co.) were dissolved in dry N,N-dimethylformamide (10 mL) and then added to the dissolved poly(vinyl alcohol).
20 The solution was stirred at 25°C. After approximately 10 minutes a white solid precipitated. The stirring was continued for 3.5 hours. The mixture was then poured into dry methanol (200 mL) and the resulting precipitate was filtered under vacuum. The solid was air dried to give 4.10
25 g of the crude polymer (66% yield). The molecular weight of the crude polymer (determined by GPC using a PL-Gel mixed pore C column; Polymer Laboratories; with different molecular weight polystyrene as standards and a refractive index detector) was found to be a mixture of weight averages
30 102,000 and 850 in a ratio of 4:1. The polymer was purified by recrystallization from boiling ethanol to give 2.50 g of the derivatized poly(vinyl alcohol). The polymer was

-30-

characterized by several analytical techniques: ^{13}C NMR, GPC, melting point.

^{13}C NMR (CDCl_3) 75.47 MHz (J-Modulated spin echo method)
5 δ 173.045 (carbonyl stearyl), δ 170.34 (carbonyl sebacoyl),
 δ 66.51 (-ve intensity, CHOH, poly(vinyl alcohol)), δ 39.50
(CH_2 , poly(vinyl alcohol)), δ 34.33 ($(\text{C}_2$, stearyl), δ 31.91
(C_3 , C_{16}), δ 29.73, 29.36 (C_6 - C_{15}), δ 24.79 (C_3), δ 22.67 (C_{17}),
 δ 14.09 (-ve intensity, C_{18}).

GPC: Weight average molecular weight ~80,500, purity
10 97%.

Melting point: Determined by differential scanning calorimetry was found to be 52-53°C.

EXAMPLE 6: Preparation of Canola oil gel

The polymer prepared as described in Example 5 was
15 incorporated into Canola oil to obtain a shortening-like
product similar to CRISCO® brand shortening. The polymer
(5% by weight) prepared as described in Example 5 was
dispersed in 45 g Canola oil. The mixture was stirring
using a magnetic stirrer and heated to a minimum of 60°C
20 (but no higher than 90 °C). The stirring was continued
until all the polymer dissolved. The resulting solution of
the polymer in Canola oil was solidified by placing the
mixture on ice for at least one hour. The gel was stored
and characterized by rheological measurements.

25 Rheological measurements of the gelled oil were
conducted on a Bohlin Visco 88 viscometer at both 4°C and
37°C. The viscosities were measured using both increasing
and decreasing shear rates. The initial viscosity (at the
lowest shear rate 21.16 sec^{-1} on the increasing rate measure-
30 ment) was used to determine the viscosity of the gelled
product. The temperature of the sample during the measure-

-31-

ment was maintained by constant temperature baths. The viscosities of the gelled Canola oil containing 5% of the polymer at 4°C and 37°C were 10.02 Pas and 5.63 Pas, respectively.

5 EXAMPLE 7: Preparation of emulsions without emulsifiers

The polymer of Example 5 was used to prepare oil continuous emulsions using liquid oil without any structured or saturated fat. The emulsions consisted of an aqueous phase which included salts and whey protein and an oil phase
10 which included the polymer. The oil phase was varied from 80-60% and the polymer from 2 to 5%. A typical formulation for 80% oil phase containing 2% of the polymer (prepared as described in Example 5) is given below:

	<u>% in Final Product</u>
<u>OIL PHASE</u>	
Canola Oil (Procter & Gamble Co.)	75
Polymer (Example 5)	5
<u>WATER PHASE</u>	
Water	18
Sodium chloride	2

The polymer was dispersed in the oil phase and heated to about 65°C (but no higher than 90°C) and mixed until all the polymer dissolved. The aqueous phase containing sodium chloride and whey protein was prepared by heating the
5 mixture with stirring to a minimum of 65°C (but no higher than 70°C) and continuing the mixing until all the solids had dissolved. When both phases had reached the appropriate temperatures, the aqueous phase was slowly poured into the stirred oil phase. The emulsion was assembled under shear
10 using a Silverson L4R (Silverson Machines Limited) for a

-32-

total of 2 minutes. Care was taken to avoid the inclusion of air in the emulsion. When the emulsification was complete, the emulsion was placed on ice and allowed to solidify for at least 1 hour.

- 5 The viscosity of the final product was measured at both 4°C and 37°C according to the procedure described in Example 6. The results are given in Table I.

TABLE I

<u>% Oil Phase in Final Phase</u>	<u>% Polymer in Final Product</u>	<u>Viscosity at 4°C (Pas)</u>	<u>Viscosity at 37°C (Pas)</u>
80	5	14.77	11.29
60	5	over range	14.12
60	2	13.37	8.32

EXAMPLE 8: Preparation of emulsions with emulsifiers

- The polymer (prepared as described in Example 5) was used to prepare oil continuous emulsions using liquid oil (without any structured or saturated fat) and emulsifiers in the oil phase. The emulsions were prepared as described in Example 7, except that a total of 9% emulsifier was included in the oil phase. A typical formulation for 89% oil phase containing 5% of the polymer (prepared as described in Example 5) is given below:

% in Final Product

OIL PHASE

Canola Oil (Procter & Gamble Co.)	75
Polymer (Example 1)	5
Span 80 (Sigms Chemical Co.)	4
Tween 80 (Spectrum Chemical Mfg. Corp.)	4
Dimodan WPC (Grinstad Products Inc.)	1

-33-

WATER PHASE

Water	10
Sodium chloride	1

The emulsion was prepared as described in Example 7. The viscosity of the oil continuous emulsion containing 80% oil phase, 5% polymer at 4°C and 37°C measured as described in Example 6 were 11.64 Pas and 7.79 Pas, respectively.

- 5 EXAMPLE 9: Synthesis of crosslinked polymer derived from poly(vinyl alcohol) molecular weight 9000-10,000, palmitoyl chloride and sebacoyl chloride.

10 Poly(vinyl alcohol), average molecular weight 9000-10,000 (220 mg, 5 mM based on vinyl alcohol; Aldrich Chemical Co.) was dissolved in dry N,N-dimethylformamide (2 mL) at 100°C. Sebacoyl chloride (12 mg, 0.05 mM; Aldrich Chemical Co.) was dissolved in dry N,N-dimethylformamide (0.5 mL) and added to the dissolved poly(vinyl alcohol).

15 The mixture was stirred at 70°C. After ~5 minutes a solution of palmitoyl chloride (1.37 g, 5 mM; Aldrich Chemical Co.) in dry N,N-dimethylformamide (1.5 mL) was added. The mixture was stirred at 70°C for 2 hours. The reaction mixture was then poured into ethanol (50 mL) and

20 the resulting precipitate was filtered under vacuum. The solid was air dried to give 1.01 g of the crude polymer (72% yield). The molecular weight of the crude polymer determined by GPC as described in Example 5 has a single peak of weight average 60,600. The polymer (without further purification)

25 cation) was used to prepare a Canola oil gel as described in Example 5. The resulting product containing 10% polymer was a gel at 4°C but liquid at 25°C.

-34-

EXAMPLE 10: Synthesis of crosslinked polymer derived from poly(vinyl alcohol) molecular weight 50,000, stearyl chloride and sebacoyl chloride.

5 A polymer derived from poly(vinyl alcohol) average molecular weight 50,000, stearyl chloride and sebacoyl chloride was synthesized by a modification of the procedure described in Example 5. Poly(vinyl alcohol), average molecular weight 50,000 (44 mg, 1 mM based on vinyl alcohol;
10 Aldrich Chemical Co.) was dissolved in dry N,N-dimethylformamide (3 mL) by heating the solution to ~150°C. A mixture of stearyl chloride (303 mg, 1 mM; Aldrich Chemical Co.) and sebacoyl chloride (2.4 mg, 0.01 mM; Aldrich Chemical Co.) were dissolved in dry N,N-dimethylformamide (2
15 mL) and then added to the dissolved poly(vinyl alcohol) at 70°C. The solution was stirred at 70°C for 1 hour. The mixture was then poured into dry ethanol (50 mL) and the resulting precipitate was filtered under vacuum. The solid was air dried and the molecular weight of the crude polymer
20 was determined by GPC as described in Example 5. The polymer was a mixture of weight averages 169,00 and 740 in a ratio of 3:1. The crude polymer was used to prepare a Canola oil gel as described in Example 6. The resulting gel containing 10% polymer was softer than the gel prepared with
25 the polymer as described in Example 5.

-35-

EXAMPLE 11: Synthesis of crosslinked polymer derived from poly(vinyl alcohol) molecular weight 50,000, palmitoyl chloride and sebacoyl chloride.

5 The polymer derived from poly(vinyl alcohol) average molecular weight 50,000, palmitoyl chloride and sebacoyl chloride was synthesized by a modification of the procedure described in Example 10. Poly(vinyl alcohol), average molecular weight 50,000 (44 mg, 1 mM based on vinyl alcohol;
10 Aldrich Chemical Co.) was dissolved in dry N,N-dimethylformamide (2 mL) by heating the solution to 140°C. A mixture of palmitoyl chloride (275 mg, 1 mM; Aldrich Chemical Co.) and sebacoyl chloride (2.4 mg, 0.01 mM; Aldrich Chemical Co.) were dissolved in dry N,N-dimethyl-
15 formamide (2 mL) and then added to the dissolved poly(vinyl alcohol) at ~140°C. The solution was then stirred at 140°C for 5 minutes and then left stirring at 70°C for 40 minutes. The mixture was then poured into dry ethanol (3 mL) and the resulting precipitate was filtered under vacuum. The solid
20 was air dried and the molecular weight of the crude polymer was determined by GPC as described in Example 5. The polymer was a mixture of weight averages 2.7×10^6 , 240,000 and 650 in a ratio of 1:13:1.4. The crude polymer was used to prepare a Canola oil gel as described in Example 6. The
25 resulting gel containing 10% polymer was softer than the gel prepared with the polymer as described in Example 5.

-36-

EXAMPLE 12: Preparation of poly(hexadecylmethacrylate)
gel using Canola oil

A solution of poly(hexadecylmethacrylate) in toluene (Aldrich Chemical Co.) was rotary evaporated under vacuum to
5 remove the solvent. The polymer was then incorporated into
Canola oil to obtain a shortening-like product similar to
CRISCO® brand shortening. The polymer (20% by weight) was
dispersed in 90 g Canola oil. The mixture was stirring
using a magnetic stirrer and heated to a minimum of 60°C
10 (but no higher than 90°C). The stirring was continued until
all the polymer dissolved. The resulting solution of the
polymer in canola oil was place on ice for at least one hour
to solidify. The product was a gel at 4°C and a liquid at
room temperature.

15 EXAMPLE 13: Preparation of poly(octadecylmethacrylate) gel
using Canola oil

A solution of poly(octadecylmethacrylate) in toluene (Aldrich Chemical Co.) was rotary evaporated under vacuum to
remove the solvent. The polymer was then incorporated into
20 Canola oil to obtain a shortening-like product similar to
CRISCO® brand shortening. The polymer (20% by weight) was
dispersed in 90 g Canola oil. The mixture was stirring
using a magnetic stirrer and heated to a minimum of 60°C
(but no higher than 90°C). The stirring was continued until
25 all the polymer dissolved. The resulting solution of the
polymer in canola oil was place on ice for at least one hour
to solidify. The product was a gel at 4°C and a liquid at
room temperature.

-37-

EXAMPLE 14: Preparation of poly(ethylene glycol 400) distearate gel using Canola oil

Poly(ethylene glycol 400) distearate (Aldrich Chemical Co.) was incorporated into Canola oil to obtain a shortening-like product similar to CRISCO® brand shortening. The polymer (20% by weight) was dispersed in 90 g Canola oil. The mixture was stirring using a magnetic stirrer and heated to a minimum of 60°C (but no higher than 90°C). The stirring was continued until all the polymer dissolved. The resulting solution of the polymer in canola oil was place on ice for at least one hour to solidify. The product was a gel at 4°C and a liquid at room temperature.

Example 15: Synthesis of alkyd-type polymer from monoglycerides and aconitic acid

Thirty-four and a half grams (34.5 g) of C22 monoglycerides derived from hydrogenated vegetable oil (PA-28, Kodak, Eastman Chemicals Division, Kingsport, TN) were placed in a roundbottom 100 mL flask and melted at 140°C. Eight grams of aconitic acid monohydrate (Sigma Chemical Company, St. Louis, MO) were then added under stirring. The above weight ratio resulted in 1/1.75 molar ratio of aconitic acid to monoglycerides. Vacuum was applied (6-10 mm Hg) and the temperature was raised to 200°C. After 3h minutes, 210 mg of phosphoric acid were added and the reaction mixture was stirred at 200°C and under vacuum for another 22 hours, forming the polymer.

The polymer was cooled to room temperature, homogenized to a powdered state and thoroughly washed with methanol to remove the catalyst. The molecular weight of the resulting polymer (determined by GPC with different MW

-38-

polystyrenes as standards) was found to be around 32,000. The product melting properties were determined by differential scanning calorimetry (DSC). The melting point was found to be about 60°C.

5 EXAMPLE 16: Preparation of a polyester gel using
a fat mimetic

The aconitic acid polymer (prepared as described in Example 15) was incorporated into the synthetic oil Sorbestrin to obtain a shortening-like product similar to
10 Crisco® brand shortening. The polymer (10% by weight) was dispersed in 45 g of a sorbitol fatty acid ester with degree of substitution of about 4. The mixture was stirring using a magnetic stirrer and heated to a minimum of 60°C (but no higher than 90°C). The stirring was continued until all of
15 the polymer dissolved. The resulting solution of the polymer in Sorbestrin was solidified by placing the mixture on ice for at least one hour. The gel was stored and characterized by rheological measurements.

Rheological measurements of the gelled oil were
20 conducted on a Bohlin Visco 88 viscometer at both 4°C and 37°C. The viscosities were measured using both increasing and decreasing shear rates. The initial viscosity (at the lowest shear rate 21.16 sec⁻¹ on the increasing rate measurement) was used to determine the viscosity of the
25 gelled product. The temperature of the sample during the measurement was maintained by constant temperature baths. The viscosities of the gelled Sorbestrin containing 10% of the polymer at 4°C and 37°C were 10.64 Pas and 8.13 Pas, respectively.

-39-

EXAMPLE 17: Preparation of Fat spread using polyester and synthetic oil

The aconitic acid polymer (prepared as described in Example 15) was used to prepare a high quality oil-continuous fat spread using the synthetic oil Sorbestrin without added structural or saturated fat or emulsifiers. The oil phase consisted of 38% Sorbestrin and 2% aconitic acid polymer. The aqueous phase included salts and whey procein. A typical formulation for 40% oil phase containing 2% of the polymer is given below:

	<u>% in Final Product</u>
<u>OIL PHASE</u>	
Sorbestrin (Pfizer, Inc.)	38
Polyester polymer	2
 <u>WATER PHASE</u>	
Water	57
Sodium chloride	2
Daritek (whey protein concentrate) (Foremost Whey Products)	1

The polymer was dispersed in the oil phase and heated to about 65°C (but not higher than 90°C) and mixed until all the polymer dissolved. The aqueous phase containing sodium chloride and whey protein was prepared by heating the mixture with stirring to a minimum of 65°C (but no higher than 70°C) and continuing the mixing until all the solids had dissolved. When both phases had reached the appropriate temperatures, the aqueous phase was slowly poured into the stirred oil phase. The emulsion was assembled under shear

-40-

using a Silverson L4R (Silverson Machines Limited) for a total of 2 minutes. Care was taken to avoid the inclusion of air in the emulsion. When the emulsification was complete, the emulsion was placed on ice and allowed to solidify for at least 1 hour. The emulsions were stored and characterized by rheological measurements as described in Example 16. The viscosity of the product at 4°C and 37°C were over range and 12.74 Pas, respectively.

10 EXAMPLE 18: Polyesters as oil thickening agents
for medium chain triglycerides

A citric acid polymer (prepared according to Example 1) was used to prepare a high quality oil continuous fat spread using liquid medium chain triglycerides without added structural or saturated fat or emulsifiers. The oil phase consisted of the 38% NEOBEE® M-5 (medium chain triglyceride, Stephan Company) and 2% citric acid polymer. The aqueous phase included slats and whey protein. A typical formulation for 40% oil phase containing 2% of the polymer is given below:

20		<u>% in Final Product</u>
	<u>OIL PHASE</u>	
	NEOBEE® M-5 (Stephan Company)	38
	Polyester polymer	2

-41-

WATER PHASE

	Water	57
	Sodium chloride	2
	Daritek (whey protein concentrate)	1
5	(Foremost Whey Products)	

The polymer was dispersed in the oil phase and herated to about 65°C (but not higher than 90°C) and mixed until all the polymer dissolved. The aqueous phase containing sodium chloride and whey protein was prepared by heating the
10 mixture with stirring to a minimum of 65°C (but no higher than 70°) and continuing the mixing until all the solids had dissolved. When both phases had reached the appropriate temperatures, the aqueous phase was slowly poured into the stirred oil phase. The emulsion was assembled under shear
15 using a Silverson L4R (Silverson Machines Limited) for a total of 2 minutes. Care was taken to avoid the inclusion of air in the emulsion. When the emulsification was complete, the emulsion was placed on ice and allowed to solidify for at least 1 hour.

20 Equivalents

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. Such equivalents are intended to be
25 encompassed by the following claims.

-42-

CLAIMS

1. An edible food product containing an oil phase thickened with a texturizing agent present in an amount sufficient to significantly increase the viscosity of the oil phase of said edible food product, said
5 texturizing agent comprising an alkyl-substituted, non-nitrogen containing oil-soluble polymer having a molecular weight of at least about 2000 daltons, wherein said oil phase is a naturally occurring oil, a synthetic oil, a fat mimetic or combinations
10 thereof.
2. An edible food product of Claim 1 wherein said polymer is selected from the group consisting of methacrylate polymers, polyglycol esters, polyvinyl alcohol esters, and polyvinyl alcohol esters crosslinked with a poly-
15 carboxylic acid.
3. An edible food product of Claim 2 wherein the oil phase comprises canola oil, soybean oil, sunflower oil, peanut oil, safflower oil, olive oil or corn oil.
4. An edible food product of Claim 2 wherein the oil
20 phase comprises hydrogenated vegetable oil, butter fat or cocoa butter.
5. An edible food product of Claim 2 wherein the polymer comprises from about 2% to about 20%, by weight, of the oil phase of said edible food product.

-43-

6. An edible emulsion comprising an aqueous phase and an oil phase thickened with a texturizing agent comprising an alkyl-substituted, non-nitrogen containing oil-soluble polymer having a molecular weight of at least about 2000 daltons, wherein said oil phase is a naturally occurring oil, a synthetic oil, or fat mimetic or combinations thereof.
7. An edible emulsion of Claim 6 wherein said polymer is selected from the group consisting of methacrylate polymers, polyglycol esters, polyvinyl alcohol esters, and polyvinyl alcohol esters crosslinked with a polycarboxylic acid.
8. An edible emulsion of Claim 6 wherein the oil phase comprises from about 20% to about 80%, by weight, of the emulsion.
9. A fat-containing food product in which all or part of the fat is substituted with an oil phase thickened with a texturizing agent present in an amount sufficient to significantly increase the viscosity of the oil phase of said edible food product, said texturizing agent comprising an alkyl-substituted, non-nitrogen containing oil-soluble polymer having a molecular weight of at least about 2000 daltons, wherein said oil phase is a naturally occurring oil, a synthetic oil, a fat mimetic or combinations thereof.

-44-

10. A food product of Claim 9 wherein said polymer is selected from the group consisting of methacrylate polymers, polyglycol esters, polyvinyl alcohol esters, and polyvinyl alcohol esters crosslinked with a polycarboxylic acid.
11. A fat-containing food product in which all or part of the fat is substituted with an oil phase thickened with a texturizing agent comprising an alkyl-substituted, non-nitrogen containing oil-soluble polymer having a molecular weight of at least about 2000 daltons, wherein said oil phase is a naturally occurring oil, a synthetic oil, a fat mimetic or combinations thereof.
12. A food product of Claim 11 wherein said polymer is selected from the group consisting of methacrylate polymers, polyglycol esters, polyvinyl alcohol esters, and polyvinyl alcohol esters crosslinked with a polycarboxylic acid.
13. An edible food spread containing an emulsion comprising an aqueous phase and an oil phase thickened with a texturizing agent comprising an alkyl-substituted, non-nitrogen containing oil-soluble polymer having a molecular weight of at least about 2000 daltons, wherein said oil phase is a naturally occurring oil, a synthetic oil, a fat mimetic or combinations thereof.

-45-

14. An edible food spread of Claim 13 wherein said polymer is selected from the group consisting of methacrylate polymers, polyglycol esters, polyvinyl alcohol esters, and polyvinyl alcohol esters crosslinked with a polycarboxylic acid.
15. A baked food product in which all or part of the hydrogenated fat normally present is substituted with an oil phase comprising an unsaturated oil thickened with a texturizing agent present in an amount sufficient to significantly increase the viscosity of the oil phase, said texturizing agent comprising an alkyl-substituted, non-nitrogen containing oil-soluble polymer having a molecular weight of at least about 2000 daltons, wherein said oil phase is a naturally occurring oil, a synthetic oil, a fat mimetic or combinations thereof.
16. A product of Claim 15 wherein said polymer is selected from the group consisting of methacrylate polymers, polyglycol esters, polyvinyl alcohol esters, and polyvinyl alcohol esters crosslinked with a polycarboxylic acid.
17. A baked food product in which all or part of the hydrogenated fat normally present is substituted with an emulsion comprising an aqueous phase and an unsaturated oil thickened with a texturizing agent comprising an alkyl-substituted, non-nitrogen containing oil-soluble polymer having a molecular weight of at least about 2000 daltons, wherein said oil phase is a naturally occurring oil, a synthetic oil, a fat mimetic or combinations thereof.

-46-

18. A product of Claim 17 wherein said polymer is selected from the group consisting of methacrylate polymers, polyglycol esters, polyvinyl alcohol esters, and polyvinyl alcohol esters crosslinked with a poly-carboxylic acid.
- 5

1 / 2

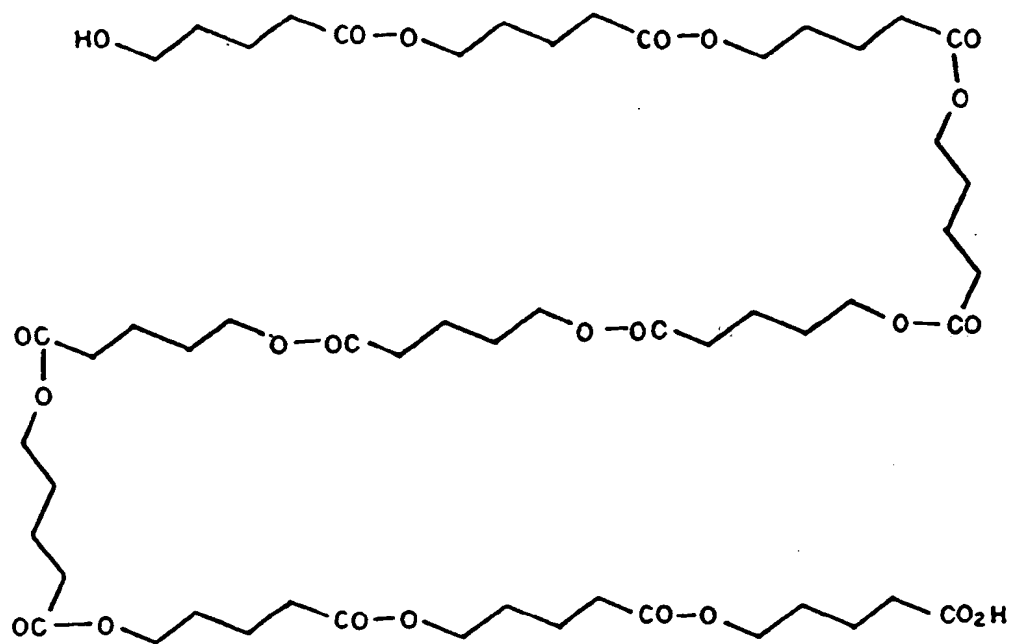


FIG. 1

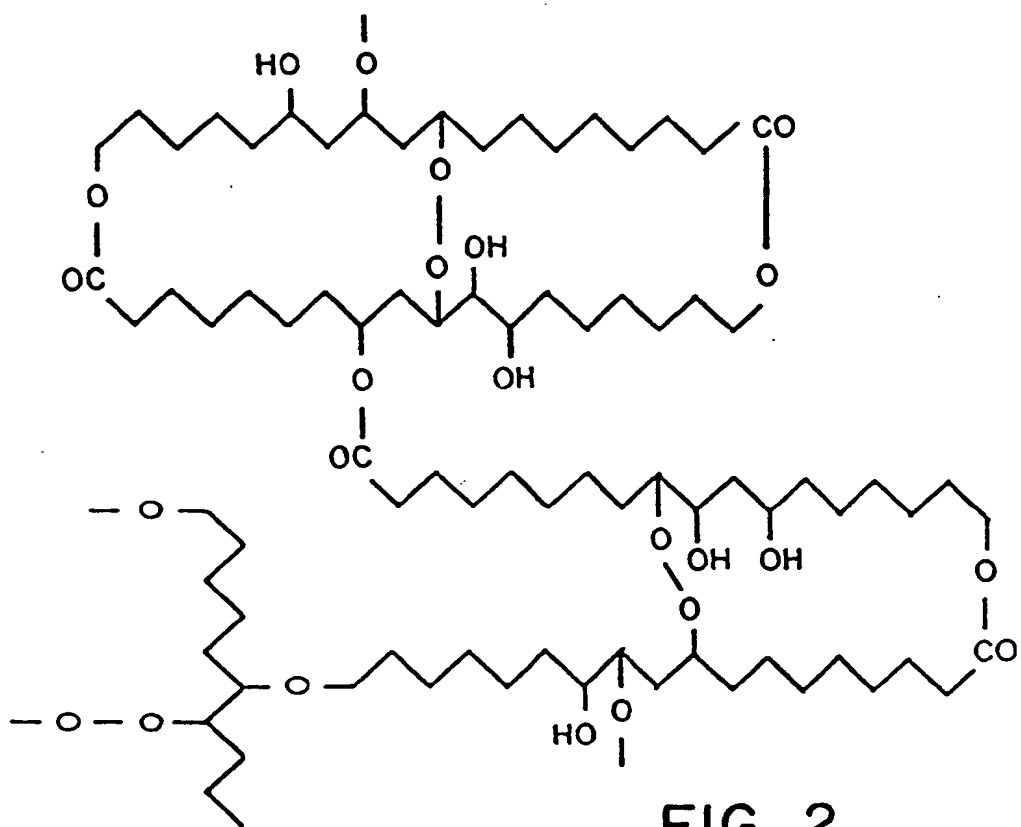
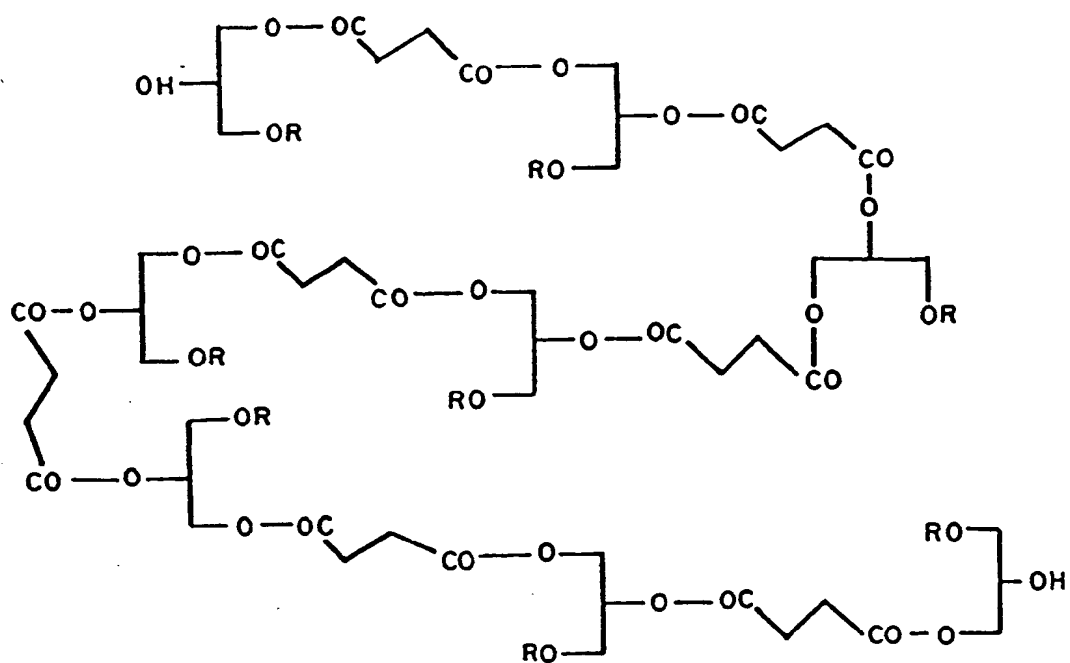


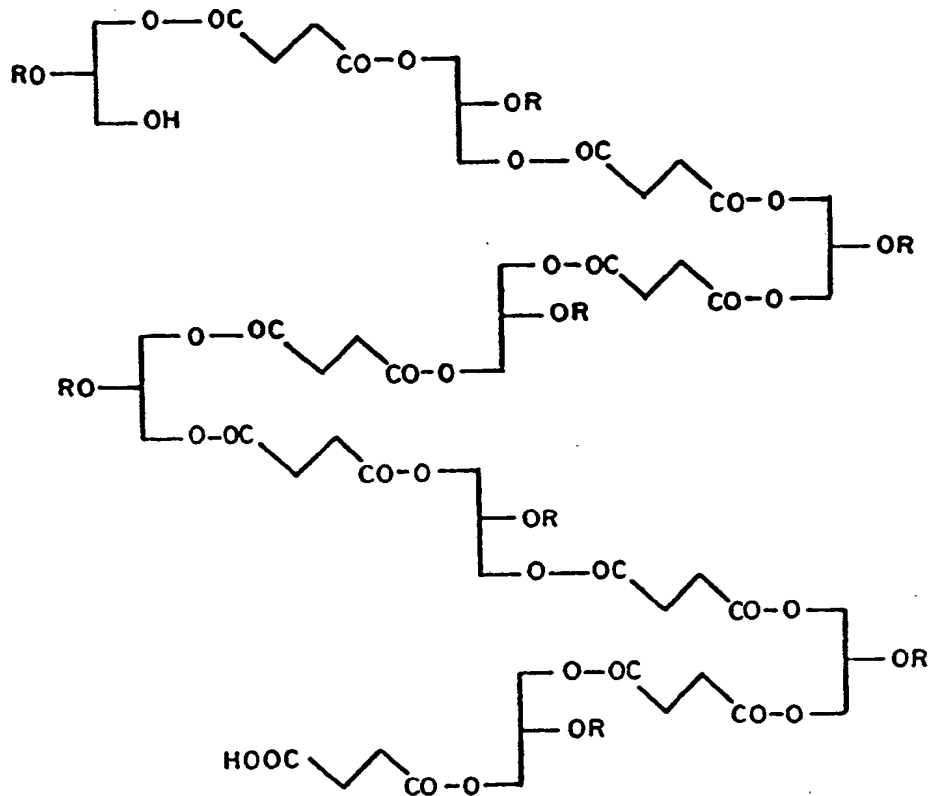
FIG. 2

2/2



$R = \text{CH}_3 - (\text{CH}_2)_n - \text{CO}-$
 $n = 14-16$

FIG. 3



$R = \text{CH}_3 - (\text{CH}_2)_n - \text{CO}-$
 $n = 14-16$

FIG. 4

INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/US 94/03567

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 A23D9/013 A23D7/00 A23D7/015 A23L1/308

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 A23D A23L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,92 03937 (OPTA FOOD INGREDIENTS INC.) 19 March 1992 see page 2 - page 3; claims 1-19,23-30; figures 1-4; examples 1-4 see page 7 - page 9 ---	1-18
X	EP,A,0 383 605 (NABISCO BRANDS INC.) 22 August 1990 see column 6, line 39 - column 7, line 5; claims 1-3,9-13,44-46,51-53,55 ---	1-4,6,7, 9-16
X	US,A,5 068 119 (NABISCO BRANDS INC.) 26 November 1991 see column 6, line 28 - line 43; claims 1,14,20; examples 7,10 ---	1-4,6-16
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

6 July 1994

Date of mailing of the international search report

25 07 94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl.
Fax (+ 31-70) 340-3016

Authorized officer

Kanbier, D

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/03567

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,92 01386 (NABISCO BRANDS INC.) 6 February 1992 see page 4; claim 1; examples 2,4,6 see page 11 ---	1-4,6-8
X	US,A,2 666 706 (E.F. DREW & CO.) 19 January 1954 see column 1 - column 3; claims 1-3; example 1 ---	1-3,5, 9-12,15, 16
X	US,A,2 610 915 (SWIFT & COMPANY) 16 September 1952 see column 1 - column 3; claim 1; example 1 ---	1-3
X	DATABASE WPI Week 8509, Derwent Publications Ltd., London, GB; AN 85-050813 & DD,A,214 986 (ADW. DER. DDR) 24 October 1984 see abstract ---	1,2,6,7, 9-12,15, 16
X	FR,A,2 113 957 (UNILEVER NV) 30 June 1972 see page 1 - page 3; claims 1,2,8,13-15; examples 1,2,26,27 ---	1-14
X	DATABASE WPI Week 7909, Derwent Publications Ltd., London, GB; AN 79-16821 & JP,A,54 008 605 (KANEBO KK) 23 January 1979 see abstract ---	1
X	DATABASE WPI Week 7519, Derwent Publications Ltd., London, GB; AN 75-31295 & JP,A,49 088 787 (KAIHATSU CHEM. INC.) 24 August 1974 see abstract -----	1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. l. Application No

PCT/US 94/03567

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9203937	19-03-92	US-A- 5137743 AU-B- 650061 AU-A- 8539191 CA-A- 2091267 EP-A- 0547147	11-08-92 09-06-94 30-03-92 08-03-92 23-06-93
EP-A-0383605	22-08-90	US-A- 4915974 CA-A- 2005752 JP-A- 2268660 US-A- 5115017 US-A- 5240996	10-04-90 17-08-90 02-11-90 19-05-92 31-08-93
US-A-5068119	26-11-91	NONE	
WO-A-9201386	06-02-92	NONE	
US-A-2666706		NONE	
US-A-2610915		NONE	
FR-A-2113957	30-06-72	GB-A- 1359639 AT-B- 320410 AU-B- 465031 AU-A- 3553671 BE-A- 775304 CH-A- 555644 DE-A, B, C 2156121 NL-A- 7113682 SE-B- 381798	10-07-74 10-02-75 18-09-75 17-05-73 12-05-72 15-11-74 18-05-72 11-04-72 22-12-75